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Dated 7 November 2002

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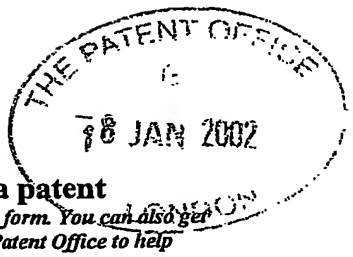

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Request for grant of a patent

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1. Your reference — C4195(C)/ijh
329

2. Patent application number *(The Patent Office will fill in this part)* — 0201165.8 — 18 JAN 2002

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

UNILEVER PLC
UNILEVER HOUSE, BLACKFRIARS
LONDON, EC4P 4BQ

Patents ADP number *(if you know it)* 76148370001

If the applicant is a corporate body, give the country/state of its incorporation — **UNITED KINGDOM**

4. Title of the invention — **AZETIDINIUM MODIFIED POLYMERS AND FABRIC TREATMENT COMPOSITION**

5. Name of your agent *(if you have one)*
"Address for Service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

ELLIOTT, Peter William
PATENT DEPARTMENT, UNILEVER PLC
COLWORTH HOUSE, SHARNBROOK
BEDFORD, MK44 1LQ

Patents ADP number *(if you know it)* 71711622001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day/month/year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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See note (d))

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Continuation sheets of this form	
Description	29
Claim(s)	3
Abstract	1
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Priority Documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature(s) Date: **18 January 2002**

Sandra EDWARDS, Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom: **Isobel Howell, Tel 01234 22 2082**

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AZETIDINIUM MODIFIED POLYMERS AND FABRIC TREATMENT COMPOSITION

Field of the Invention

The invention relates to a self-crosslinking polymer functionalised with azetidinium groups and to a fabric treatment composition which comprises the polymer. The invention further relates to the use in a domestic washing cycle or a tumble dryer of said composition.

Background of the Invention

A broad range of textile material treatments are known which involve the use of polymeric materials, both for treatment of textile materials in the form of whole cloth and in the form of finished garments. Some of these polymers are substantive. Many of these treatments are used in the garment supply chain to modify the 'finish' of garments.

Polyamide-epichlorohydrin (PAE) resins are one particular class of materials which are known for the treatment of both keratinaceous and cellulosic materials. PAE resins are also well-known in the paper industry as alkaline curing wet-strength resins.

The epichlorohydrin resins are sometimes referred to below as amine-epichlorohydrin resins and polyamine-

epichlorohydrin (PAE) resins (the two terms being used synonymously) although these terms encompass both the amine and amide resins of the invention and their derivatives. The resins may also have a mixture of amine and amide groups.

The amine- or amide-epichlorohydrin resins may have one or more functional groups capable of forming azetidinium groups and/or one or more azetidinium functional groups. Alternatively, or additionally, the resins may have one or more functional groups that contain epoxide groups or derivatives thereof e.g. Kymene™ 450 (ex Hercules). Both of these classes of resin can cross-link or react with substrates as a result of the functional groups. During the curing reaction, covalent bonds are formed between polymers and fibres and between polymer molecules themselves.

It has been determined that the use of self-crosslinking polymers bearing the azetidinium group can impart many benefits to fabrics containing cellulosic materials (e.g. cotton). These benefits include improved wear resistance, reduced pilling, improved colour definition, reduced wrinkling and improved perfume longevity.

JP 07324284 A2 describes the use of PAE resins for the treatment of wool, whereas WO 9207124 A1 describes the use of PAE resins on regenerated cellulose to reduce fibrillation. WO 9742287 A1, WO 9829530 A2 and US 6140292 A1 (P&G) describe the use of PAE resins in a laundry detergent to impart appearance benefits to garments. WO 0008127 A1

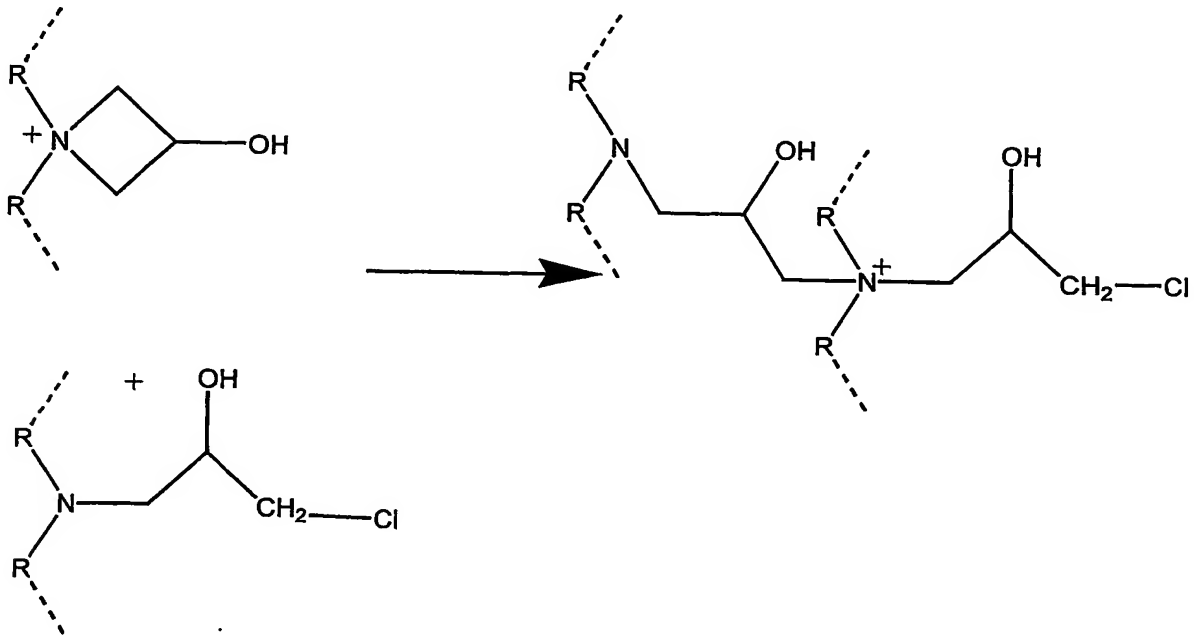
describe the use of PAE resins in a laundry powder as wrinkle-reducing agents. WO 0015747 A1, WO 0015748 A1 describe the use of PAE resins in laundry rinse products to impart various benefits (appearance, wrinkle-reduction) to garments. WO 0015755 A1 and US 6277810 B1 describes the use of PAE resins delivered in the tumble dryer to impart appearance benefits to garments.

However, the polyamidoamide-epichlorohydrin resins, available under the commercial trade names Kymene™ (Hercules), Kenores™ (Eka Nobel) have a potential to cause problems in textile applications. The crosslinking reaction leaves the treated materials positively charged. This can cause fugitive dyes to be absorbed onto said fabric leading to unwanted changes in appearance. The cationic charge can also make certain stains more difficult to remove, as the polymers tend to bind the stain to the surface.

It is believed that the reason for the above-mentioned problems is that the PAE molecule only contains secondary amines. When a polyamine is treated with epichlorohydrin according to a typical method to produce an azetidinium derivative, 50% of these secondary amines are converted into cationic azetidinium groups and 35% are converted into gamma-epichlorohydrin groups. The remaining 15% of the amines cross-link and hence become tertiary. The consequence of this is that there are no secondary amines remaining.

During the internal cross-linking reaction between an azetidinium group and a gamma epichlorohydrin the

azetidinium ring opens leaving a tertiary nitrogen but the corresponding epichlorohydrin is converted to a cationic, quaternary group. Thus the overall charge on the polymer is unchanged. The mechanism is illustrated below.



Brief Description of the Invention

We have determined that improved polymers can be made which have secondary or primary nitrogen atoms available for a cross-linking reaction with the azetidinium group.

Accordingly, the first aspect of the invention comprises an azetidinium functionalised polymer containing primary and/or secondary amine groups.

Cross-linking reactions between the azetidinium group and primary or secondary amine groups does not form quaternary groups and consequently does not result in a charged, cross-linked polymer. This lack of charge is believed to substantially reduce the problems of stain fixing and dye adsorption.

Further benefits are obtained if the polymer is synthesised from acrylate-functional monomers, thereby allowing further functionality to be incorporated into the polymer.

Accordingly, a second aspect of the present invention subsists in a azetidinium functionalised polymer of which the monomers comprise:

a) an amino-acrylate and/or amino-alkacrylate monomer, and,

b) optionally, further non-amino acrylate and/or alkacrylate monomer.

Typically, the polymers are epihalohydrin modified to form azetidinium groups.

A third aspect of the present invention provides a textile treatment composition which comprises a azetidinium functionalised polymer in accordance with the first or

second aspect of the invention and a textile compatible carrier.

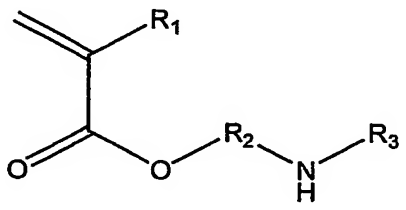
Typical concentrations of the polymers according to the invention in the final product will be such as to give 0.01-1%wt, preferably 0.1-0.2%wt on weight of textile material being treated. Typically products will contain 0.5-10%wt of polymer on product.

Detailed Description of the Invention

The polymer is preferably synthesised from an amine-containing acrylate or alkyl-acrylate monomer, with or without other monomers which do not contain an amine. Polymers formed form these monomers have pendant primary or secondary amine groups.

The amine-containing polymers:

The preferred amine/acrylate monomers have the general structure given below:



where

R_1 is hydrogen or a C_1-C_6 alkyl,

R_2 is C_1-C_6, alkyl, alkoxy or repeating units thereof, typically C2 alkyl, and,
R_3 is hydrogen or C_1-C_6 alkyl, alkoxy or repeating units thereof.

Typically R_1 will be hydrogen or methyl, i.e. the monomer will be an acrylate or methacrylate. Typically R_2 will be a two-carbon unit. While the substituents R_2 and R_3 can comprise alkoxy repeat units, such as glycol ether it is preferable that both are saturated alkyl chains. These alkyl chains may be linear or branched.

In this class of molecules the nature of the R_3 substituent will determine whether the polymer has pendant primary or secondary amine groups. Where the substituent is hydrogen then the polymer will have pendant primary amines, otherwise the pendant group will be secondary.

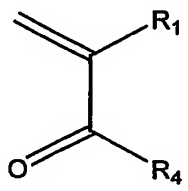
Non-limiting examples of suitable amine-containing acrylate monomers for the polymers of the invention include 2-Aminoethyl methacrylate. In this case R1 is methyl, R2 is ethyl and R3 is hydrogen. This monomer will give pendant primary amine groups when polymerised.

A further example of a suitable monomer is 2-(*tert*-butylamino)ethyl methacrylate. In this case R1 is methyl, R2 is ethyl and R3 is t-butyl. In this case the pendant amines will be secondary.

The polymer can be synthesised from a single type of amine-containing monomer or from a mixture of monomers of different structures.

Non-amine acrylate monomers:

Choice of the other (non-amine) monomers enables additional functionality to be added to the polymers. Preferred added functionality includes one or more of improved water solubility, the ability to confer softness to a textile and/or stain/soil repellence. Preferably, the monomers will be of the general formula given below:



Where:

R_1 is hydrogen or a C_1-C_6 alkyl, alkoxy or repeat units thereof

R_4 is a functional group does not contain an amine.

As with the amine monomers discussed above, R_1 will typically be hydrogen or methyl, i.e. the monomer will be an acrylate or methacrylate.

By varying R_4 it is possible to modify the features of the polymer.

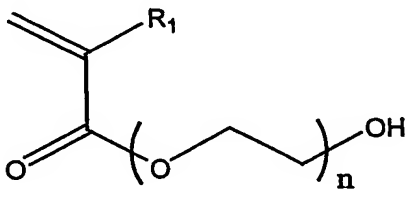
When the R_4 group is polar, such as a polyalkylene glycol, the polymer is more water soluble.

When the R_4 group is oily, such as a silicone/siloxane or a fatty chain, the polymer has softening properties.

When the R_4 group is relatively unreactive, such as a fluorocarbon the polymer confers stain and soil repellence properties.

Mixture of non-amine monomers may be employed to give some or all of these features. Non-limiting examples of suitable monomers are given below.

For water-soluble polymers R_4 can be poly(ethyleneglycol) and typical monomers are poly(ethyleneglycol) (meth)acrylates, of the general structure given below:



Where R1 is hydrogen or methyl and n is 2-20.

Other monomers which would improve the water-solubility of the polymer include poly(propylene glycol) methacrylate, poly(ethylene glycol) acrylate and poly(propylene glycol) acrylate. As in the case of the monomer described above, n will typically be 2-20.

For added softness R_4 can be poly(dimethyl siloxane) mono-methacrylate and/or poly(ethylene glycol) behenyl ether methacrylate

~~For stain/soil repellancy~~ R_4 can be one or more of 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate, 2,2,3,3,4,4,5,5-Octafluoropentyl methacrylate, 2,2,3,3,4,4-Hexafluorobutyl acrylate, 2,2,3,3,4,4-Hexafluorobutyl methacrylate, 1,1,3,3,5,5-Hexafluoroisopropyl acrylate, and, 1,1,3,3,5,5-Hexafluoroisopropyl methacrylate.

The molar ratio of the amine to non-amine monomers is typically in the range 1:10 to 10:1. Preferred polymers have molar ratio's of 5:1 to 1:5, most preferably around 1:1.

Carriers and Product Form

The compositions of this invention, when applied to a fabric, may be cured by a domestic curing step including ironing and/or tumble drying, preferably tumble drying. Preferably, these curing steps are carried out at temperatures in the range 60 to 100°C, more preferably from 80 to 100°C.

The compositions of the invention may be used before, during or after a conventional laundry process and are preferably packaged and labelled as such. The laundry process includes

large and small processes, and is preferably a domestic process.

Typically, the polymers of the invention will be used in conjunction with a textile compatible carrier.

In the context of the present invention the term "textile compatible carrier" is a component which can assist in the interaction of the polymer with the textile. The carrier can also provide benefits in addition to those provided by the first component e.g. softening, cleaning etc. The carrier may be a detergent-active compound or a textile softener or conditioning compound or other suitable detergent or textile treatment agent.

In a washing process, as part of a conventional textile washing product, such as a detergent composition, the textile-compatible carrier will typically be a detergent-active compound. Whereas, if the textile treatment product is a rinse conditioner, the textile-compatible carrier will be a textile softening and/or conditioning compound.

If the composition of the invention is to be used before, or after, the laundry process it may be in the form of a spray or foaming product.

The polymer is preferably used to treat the textile in the rinse cycle of a laundering process. The rinse cycle preferably follows the treatment of the textile with a detergent composition.

Detergent Active Compounds:

If the composition of the present invention is itself in the form of a detergent composition, the textile-compatible carrier may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof.

Many suitable detergent active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred textile-compatible carriers that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

Anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkylsulphates, particularly C_8-C_{15} primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_8-C_{20} aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C_{10}-C_{15} primary and secondary aliphatic alcohols

ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Cationic surfactants that may be used include quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein the R groups are independently hydrocarbyl chains of C_1-C_{22} length, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising cation (for example, compounds in which R_1 is a C_8-C_{22} alkyl group, preferably a C_8-C_{10} or C_{12}-C_{14} alkyl group, R_2 is a methyl group, and R_3 and R_4, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters) and pyridinium salts.

The total quantity of detergent surfactant in the composition is suitably from 0.1 to 60 wt% e.g. 0.5-55 wt%, such as 5-50wt%.

Preferably, the quantity of anionic surfactant (when present) is in the range of from 1 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 3 to 35% by weight, e.g. 5 to 30% by weight.

Preferably, the quantity of nonionic surfactant when present is in the range of from 2 to 25% by weight, more preferably from 5 to 20% by weight.

Amphoteric surfactants may also be used, for example amine oxides or betaines.

Builders:

The compositions may suitably contain from 10 to 70%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

The detergent composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

The aluminosilicate may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50%. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_2O.\ \ Al_2O_3.\ \ 0.8\text{-}6\ \ SiO_2$$

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Textile Softening and/or Conditioner Compounds:

If the composition of the present invention is in the form of a textile conditioner composition, the textile-compatible carrier will be a textile softening and/or conditioning compound (hereinafter referred to as "textile softening compound"), which may be a cationic or nonionic compound.

The softening and/or conditioning compounds may be water insoluble quaternary ammonium compounds. The compounds may be present in amounts of up to 8% by weight (based on the total amount of the composition) in which case the compositions are considered dilute, or at levels from 8% to about 50% by weight, in which case the compositions are considered concentrates.

Compositions suitable for delivery during the rinse cycle may also be delivered to the textile in the tumble dryer if used in a suitable form. Thus, another product form is a composition (for example, a paste) suitable for coating onto, and delivery from, a substrate e.g. a flexible sheet or sponge or a suitable dispenser during a tumble dryer cycle.

Suitable cationic textile softening compounds are substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C_{20}. More preferably, softening compounds comprise a polar head group and two alkyl or alkenyl chains having an average chain

length greater than or equal to C_{14}. Preferably the textile softening compounds have two, long-chain, alkyl or alkenyl chains each having an average chain length greater than or equal to C_{16}.

Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C_{18} or above. It is preferred if the long chain alkyl or alkenyl groups of the textile softening compound are predominantly linear.

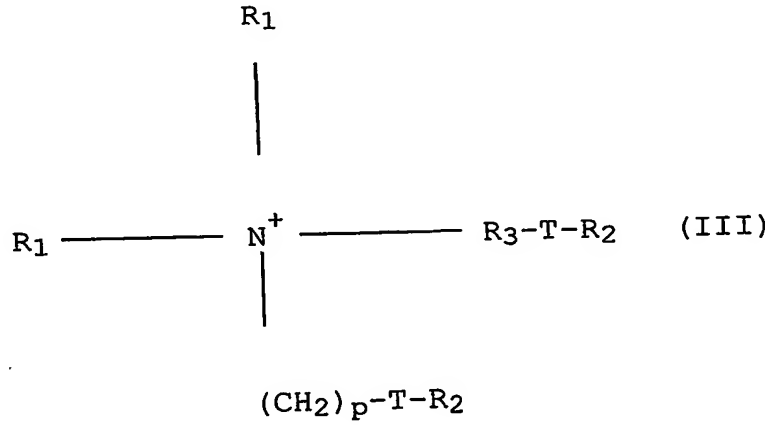
Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. Any of the conventional types of such compounds may be used in the compositions of the present invention.

The textile softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting Lβ to Lα transition temperature greater than 25°C, preferably greater than 35°C, most preferably greater than 45°C. This Lβ to Lα transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

Substantially water-insoluble textile softening compounds are defined as textile softening compounds having a

solubility of less than 1×10^{-3} wt % in demineralised water at 20°C. Preferably the textile softening compounds have a solubility of less than 1×10^{-4} wt%, more preferably less than 1×10^{-8} to 1×10^{-6} wt%.

Especially preferred are cationic textile softening compounds that are water-insoluble quaternary ammonium materials having two C_{12-22} alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. An especially preferred ester-linked quaternary ammonium material can be represented by the formula below:



(III)

wherein each R_1 group is independently selected from C_{1-4} alkyl or hydroxyalkyl groups or C_{2-4} alkenyl groups; each R_2 group is independently selected from C_{8-28} alkyl or alkenyl

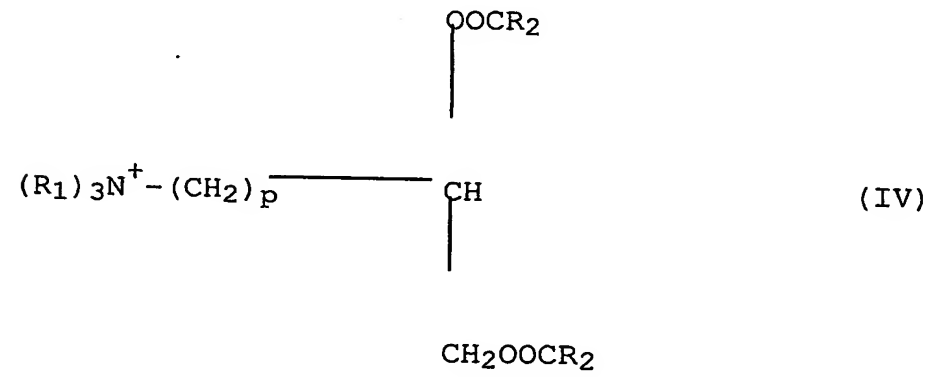
groups; and wherein R_3 is a linear or branched alkylene group of 1 to 5 carbon atoms, T is

$$-O-\overset{O}{\overset{\|}{C}}- \text{ or } -\overset{O}{\overset{\|}{C}}-O-;$$

and *p* is 0 or is an integer from 1 to 5.

Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue are especially preferred of the compounds of this type.

A second preferred type of quaternary ammonium material can be represented by the formula below:



(IV)

wherein R_1, *p* and R_2 are as defined above. It is advantageous if the quaternary ammonium material is biologically biodegradable. Preferred materials of this class such as 1,2-bis(hardened tallowoyloxy)-3-trimethylammonium propane chloride and their methods of preparation are, for example,

described in US 4 137 180 (Lever Brothers Co). Preferably these materials comprise small amounts of the corresponding monoester as described in US 4 137 180, for example, 1-hardened tallowoyloxy-2-hydroxy-3-trimethylammonium propane chloride.

Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

The compositions may alternatively or additionally contain water-soluble cationic textile softeners, as described in GB 2 039 556B (Unilever).

The compositions may comprise a cationic textile softening compound and an oil, for example as disclosed in EP-A-0829531.

The compositions may alternatively or additionally contain nonionic textile softening agents such as lanolin and derivatives thereof.

Lecithins are also suitable softening compounds.

Nonionic softeners include Lβ phase forming sugar esters (as described in M Hato et al Langmuir 12, 1659, 1666, (1996)) and related materials such as glycerol monostearate or sorbitan esters. Often these materials are used in conjunction with cationic materials to assist deposition (see, for example, GB 2 202 244). Silicones are used in a

similar way as a co-softener with a cationic softener in rinse treatments (see, for example, GB 1 549 180).

The compositions may also suitably contain a nonionic stabilising agent. Suitable nonionic stabilising agents are linear C_8 to C_{22} alcohols alkoxylated with 10 to 20 moles of alkylene oxide, C_{10} to C_{20} alcohols, or mixtures thereof.

Advantageously the nonionic stabilising agent is a linear C_8 to C_{22} alcohol alkoxylated with 10 to 20 moles of alkylene oxide. Preferably, the level of nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

The composition can also contain fatty acids, for example C_8 to C_{24} alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C_{16} to C_{18} fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1%

to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

Textile Treatment Products

The composition of the invention may be in the form of a liquid, solid (e.g. powder or tablet), a gel or paste, spray, stick or a foam or mousse. Examples include a soaking product, a rinse treatment (e.g. conditioner or finisher) or a main-wash product. The composition may also be applied to a substrate e.g. a flexible sheet or used in a dispenser which can be used in the wash cycle, rinse cycle or during the dryer cycle.

Liquid compositions may also include an agent which produces a pearlescent appearance, e.g. an organic pearlising compound such as ethylene glycol distearate, or inorganic pearlising pigments such as microfine mica or titanium dioxide (TiO_2) coated mica.

Liquid compositions may be in the form of emulsions or emulsion precursors thereof.

Composition may comprise soil release polymers such as block copolymers of polyethylene oxide and terephthalate.

Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH

buffering agents, and perfumes (preferably from 0.1 to 5% by weight).

Further optional ingredients include non-aqueous solvents, perfume carriers, fluorescers, colourants, hydrotropes, antifoaming agents, antiredeposition agents, enzymes, optical brightening agents, opacifiers, dye transfer inhibitors.

In addition, compositions may comprise one or more of anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-oxidants, UV absorbers (sunscreens), heavy metal sequestrants, chlorine scavengers, dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. The lists of optional components are not intended to be exhaustive.

In order that the invention may be further and better understood it will be described below with reference to several non-limiting examples.

Examples

Polymers were synthesised using the following methods

Example 1: ***Preparing aminoethylmethacrylate hydrochloride.***

A 500 ml 2 neck round bottomed flask was charged with 2-aminoethanol hydrochloride (46.2 g, 0.47m) and methacryloyl

chloride (49.11 g, 0.47 mols). To this hydroquinone (1mol%, 0.5g) was added to prevent polymerisation. The fused mass was then heated to 85-100°C with cautious stirring until no more hydrogen chloride evolved (12h). The amino ester hydrochloride formed was recrystallised from dry dichloroethane and vacuum dried to give a white crystalline solid (63 g, 84%).

(δH 500MHz; $CDCL_3$) 1.95 (3H, s, CH_3) 3.66 (2H, m, $-CH_2-$) 4.5 (2H, t, J 5 Hz, $-CH_2-$) 5.62 (H, s, vinyl CH) 6.27 (H, s, vinyl CH) 8.38 (3H, bs, NH_3^+).

Example 2: ***Polymerising aminoethylmethacrylate hydrochloride with oligoethyl-methacrylate monomethyl ether (M.wt. 430) 1:1 molar ratio.***

Aminoethylmethacrylate hydrochloride (5 g, 0.03 mols, 1 equivalent), oligoethylmethacrylate monomethyl ether (M. wt. 430)(13 g, 0.03 mols 1 equivalent) and AIBN (0.18 g, 1 % w/w) were dissolved in water (180 ml). The solution was degassed via the freeze-pump-thaw method and purged with nitrogen. The flask was sealed and the solution stirred with heating at 80°C for 12 hours. The polymer solution was then freeze dried and the polymer re-dissolved in THF. This organic solution was then added dropwise to vigorously stirring chilled (-20 °C) hexane to give the polymer as a white precipitate. The precipitate was then filtered off and washed with a further amount of chilled non-solvent to give a clear sticky polymer (16.9 g, 94 %).

Example 3: ***Functionalisation with epichlorohydrin.***

The previously prepared polymer of example 2 (2 g, 2.88 mmol equivalents based on amine level) was dissolved in water (20 ml) and basified with NaOH solution until pH 10. Epichlorohydrin (0.27 g, 2.88 mmols, 1 equivalent) was added to the solution and stirring was continued at room temperature for either 2 or 4 hours before the solution was acidified with HCl solution to pH 4.

Example 4: ***Polymerisation of aminoethylmethacrylate hydrochloride with oligoethyl-methacrylate monomethyl ether (M. wt. 430) 1:1 molar ratio with chain transfer agent.***

Aminoethylmethacrylate hydrochloride (5 g, 0.03 mols, 1 equivalent), oligoethylmethacrylate monomethyl ether (M. wt. 430) (13 g, 0.03 mols 1 equivalent), butane thiol (0.045 g, 0.25 % w/w) and AIBN (0.18 g, 1 % w/w) were dissolved in water (180 ml). The solution was degassed via the freeze-pump-thaw method and purged with nitrogen. The flask was sealed and the solution stirred with heating at 80°C for 12 hours. The polymer solution was then freeze dried and the polymer re-dissolved in THF. This organic solution was then added dropwise to vigorously stirring chilled (-20 °C) hexane to give the polymer as an off-white precipitate. The precipitate was then filtered off and washed with a further amount of chilled non-solvent to give a clear viscous polymer (15.1 g, 84 %).

Example 5: ***Polymerising 2-tert-butylaminoethyl methacrylate with oligoethylmethacrylate monomethyl ether (M. wt. 430) 1:1 molar ratio.***

2-*tert*-butylaminoethyl methacrylate (5g, 27 mmols, 1 equivalent), oligoethylmethacrylate monomethyl ether (M. wt. 430) (11.6 g, 27 mmols 1 equivalent) and AIBN (0.16 g, 1 % w/w) were dissolved in anhydrous THF (160 ml). The solution was degassed via the freeze-pump-thaw method and purged with nitrogen. The flask was sealed and the solution stirred with heating at 60°C for 12 hours.

The solution was then concentrated under vacuum and added dropwise to vigorously stirring chilled (-20 °C) hexane to give the polymer as a white precipitate. The precipitate was then filtered off and washed with a further amount of chilled non-solvent to give a clear sticky polymer (14.95 g, 91 %).

Example 6: ***Polymerisation of 2-tert-butylaminoethyl methacrylate with oligoethylmethacrylate monomethyl ether (M. wt. 430) 1:2 molar ratio with chain transfer agent.***

2-*tert*-butylaminoethyl methacrylate (5g, 27 mmols, 1 equivalent), oligoethylmethacrylate monomethyl ether (M. wt. 430) (23.2 g, 54 mols 2 equivalents), dodecanethiol (0.28 g, 1 %w/w) and AIBN (0.28 g, 1 % w/w) were dissolved in anhydrous THF (280 ml). The solution was degassed via the freeze-pump-thaw method and purged with nitrogen. The flask

was sealed and the solution stirred with heating at 60 °C for 12 hours. The solution was then concentrated under vacuum and added dropwise to vigorously stirring chilled (-20 °C) hexane to give the polymer as clear oil. The precipitate was then filtered off and washed with a further amount of chilled non-solvent to give a clear viscous polymer (18.2 g, 65 %).

Example 7: ***Functionalisation with epichlorohydrin.***

The previously prepared polymers (2 g, 3.2 mmol equivalents based on amine level) was dissolved in water (20 ml). Epichlorohydrin (0.3 g, 3.2 mmols, 1 equivalent) was added to the solution and stirring was continued at room temperature for either 2 or 4 hours before the solution was acidified with HCl solution to pH 4.

Example 8: ***Fabric Treatment with homopolymer of 2-aminoethyl methacrylate (Epichlorohydrin:amine ratio 1:1).***

The polymer was pad-applied at 1% o.w.f. at pH 8.4 to a printed cellulosic fabric, dried at 110°C for 10 minutes. The fabric, along with an untreated control, was subjected to repeated washing in a Quickwash™ testing machine.

After one hour, the fabric was removed and the deterioration in colour measured on a Datacolor Microflash™ 200d spectrophotometer. Standard deviation shown in brackets.

Untreated fabric	red ΔE	9.96 (0.54)
	black ΔE	13.61 (0.42)
Treated fabric	red ΔE	8.38 (0.53)
	black ΔE	12.23 (0.70)

The lower values of ΔE for the treated cloth show that its properties have been improved by the treatment.

Example 9: ***Fabric Treatment with copolymer of 2-(tert-butylamino)ethyl methacrylate and poly(ethylene glycol) methacrylate, monomer ratio 1:3 (epichlorohydrin:amine ratio 1:2)***

The test performed was as in Example 8. The following results were obtained.

Untreated fabric	red ΔE	7.01 (0.42)
	black ΔE	10.40 (0.31)
Treated fabric	red ΔE	4.83 (0.26)
	black ΔE	7.64 (0.49)

Example 10: ***Paper treatment with copolymer of 2-(tert-butylamino)ethyl methacrylate and poly(ethylene glycol) methacrylate, monomer ratio 1:3 (epichlorohydrin:amine ratio 1:2)***

Pad-applied to paper at 1% o.w.f. at pH 8.4 and dried at 110°C for ten minutes. The paper was then soaked in water

and the tensile strength measured on a Testometric AX350 Universal Tester. An untreated sample was used as control.

Untreated paper	0.450 kgf (0.011)
Treated paper	0.574 kgf (0.022)

Example 11: ***Fabric treatment with copolymer of 2-(tert-butylamino)ethyl methacrylate and poly(ethylene glycol) methacrylate, monomer ratio 1:99. (epichlorohydrin:amine ratio 1:2).***

The test used was the same as the test in Example 8. The following results were obtained.

Untreated fabric	red ΔE	7.98 (0.49)
	black ΔE	10.38 (0.41)
Treated sample	red ΔE	6.99 (0.25)
	black ΔE	8.97 (0.52)

Example 12: ***Fabric treatment with copolymer of 2-Aminoethyl methacrylate and poly(ethylene glycol) methacrylate, monomer ratio 5:95. (epichlorohydrin:amine ratio 1:1).***

The test used was the same as the test in Example 8. The following results were obtained.

Untreated fabric	red ΔE	7.97 (0.24)
	black ΔE	11.29 (0.38)
Treated fabric	red ΔE	7.20 (0.33)
	black ΔE	11.12 (0.45)

CLAIMS

1. An azetidinium functionalised polymer containing primary or secondary amine groups.

2. An azetidinium functionalised polymer according to claim 1 of which the monomers comprise:

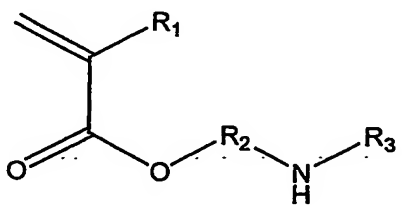
   a) an amino-acrylate and/or amino-alkacrylate monomer, and,

   b) optionally, further non-amino acrylate and/or alkacrylate monomers.

3. A textile treatment composition which comprises a polymer in accordance with claim 1 or claim 2 and a textile compatible carrier.

4. A textile treatment composition according to claim 3 wherein the concentration of the polymer is such as to give 0.01-1%wt on weight of textile material being treated.

5. A polymer according to claim 2 wherein the amine containing acrylate monomers have the general structure:



wherein:

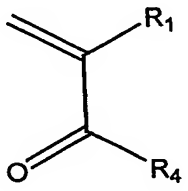
R_1 is hydrogen or a C_1-C_6 alkyl,

R_2 is C_1-C_6, alkyl, alkoxy or repeating units thereof, and,

R_3 is hydrogen or C_1-C_6 alkyl, alkoxy or repeating units thereof.

6. A polymer according to claim 5 wherein the amine containing acrylate monomers include one or more of 2-Aminoethyl methacrylate, and, 2-(*tert*-butylamino)ethyl methacrylate.

7. A polymer according to claim 2 wherein the non-amino acrylate and/or alkacrylate monomers are of the general



formula:

where:

R_1 is hydrogen or a C_1-C_6 alkyl, alkoxy or repeat units thereof,

R_4 is a functional group does not contain an amine.

8. A polymer according to claim 7 wherein R_4 is a polyalkyleneglycol.

9. A polymer according to claim 8 wherein the non-amino monomer is one or more of
poly(ethyleneglycol)methacrylate,
poly(propyleneglycol)methacrylate,
poly(ethyleneglycol)acrylate, and,
poly(propylene glycol)acrylate.

10. A polymer according to claim 7 wherein R_4 is poly(dialkyl siloxane) or poly(alklene glycol) fatty ether.

11. A polymer according to claim 7 wherein R_4 is one or more of one or more of:
2,2,3,3,4,4,5,5-Octafluoropentyl acrylate,
2,2,3,3,4,4,5,5-Octafluoropentyl methacrylate,
2,2,3,3,4,4-Hexafluorobutyl acrylate,
2,2,3,3,4,4-Hexafluorobutyl methacrylate,
1,1,3,3,5,5-Hexafluoroisopropyl acrylate, and,
1,1,3,3,5,5-Hexafluoroisopropyl methacrylate.

ABSTRACT

AZETIDINIUM MODIFIED POLYMERS AND FABRIC TREATMENT COMPOSITION

The invention relates to a fabric treatment composition which comprises a self-crosslinking polymer possessing pendant azetidinium groups. A first aspect of the invention comprises an azetidinium functionalised polymer containing primary or secondary amine groups.

Cross-linking reactions between the azetidinium group and primary or secondary amine groups does not form quaternary groups and consequently does not result in a charged, cross-linked polymer. This lack of charge is believed to overcome the problems of stain fixing and dye adsorption. A second aspect of the present invention subsists in a azetidinium functionalised polymer of which the monomers comprise: an amino-acrylate and/or amino-alkacrylate monomer, and, optionally, further non-amino acrylate and/or alkacrylate monomer. A third aspect of the present invention provides a textile treatment composition which comprises a azetidinium functionalised polymer in accordance with the first or second aspect of the invention and a textile compatible carrier.